

AN ADIABATIC CALORIMETER
FOR HEAT CAPACITIES AT
LOW TEMPERATURES

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

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JOHN CAMPBELL SOUTHARD

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The author wishes to express his appreciation to Associate Professor Donald H. Andrews not only for his suggestion and supervision of this problem but also for his interest and encouragement. He wishes to acknowledge the help received in lectures and conferences from Professors Frazer, Patrick and Reid; Associate Professors Cartledge and Rice; and Drs. Ott, Thornton and Taylor.



THE HEAT CAPACITIES OF ORGANIC COMPOUNDS AT
LOW TEMPERATURES. III. AN ADIABATIC CALORIM-
ETER FOR HEAT CAPACITIES AT LOW
TEMPERATURES.¹

BY

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IN 1909 Eucken,² working in Nernst's laboratory, devised an apparatus for the measurement of specific heats at low temperatures in which the substance itself acted as the calorimeter. A block of the material in question was suspended in a vacuum to provide thermal insulation, measured quantities of energy were added electrically and the rise in temperature observed by a resistance thermometer or a thermocouple. Corrections had to be made for radiation and other heat leaks. At temperatures below the boiling point of liquid air these were quite small but at higher temperatures they amounted to so much that observations were not very accurate.

This trouble has been corrected to some extent by Nernst and Schwes³ and to a greater extent by Gibson and Giauque,⁴ and by Andrews,⁵ and others by using shields of various sorts which keep the temperature of the surroundings in the neighborhood of that of the calorimeter. Obviously, the ideal condition would be when the temperature of the shield is kept at exactly the temperature of the calorimeter at all times. In other words, the process should be adiabatic. The present work is an attempt to do just this, and while certain modifications are perhaps desirable, we believe it shows definitely

¹ From the dissertation submitted by J. C. Southard in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² *Physik Z.*, **10**: 586 (1909).

³ Nernst and Schwes, *Sitz. Ber. Preuss. Akad. Wiss.*, 355 (1914).

⁴ Gibson and Giauque, *J. A. C. S.*, **45**: 93 (1923).

⁵ Andrews, *JOURNAL OF THE FRANKLIN INSTITUTE*, **206**: 285 (1929).

that it is possible to approach such an optimum condition closely enough to give consistent results. At the same time there are other advantages to be found in this method. It is more rapid, due largely to the fact that it is a continuous process without any tedious wait after heating while the substance comes to thermal equilibrium. The calculation of results is much simpler as there are no corrections to be made for heat leaks, radiation and so on. It is economical, taking about one liter of liquid air for a run and using a standard quart dewar. Furthermore, the great majority of compounds can be obtained pure in the 10 gram samples required here but not in quantities of fifty grams or more which must be generally used for the successful operation of the Nernst type calorimeter.

DESCRIPTION OF APPARATUS.

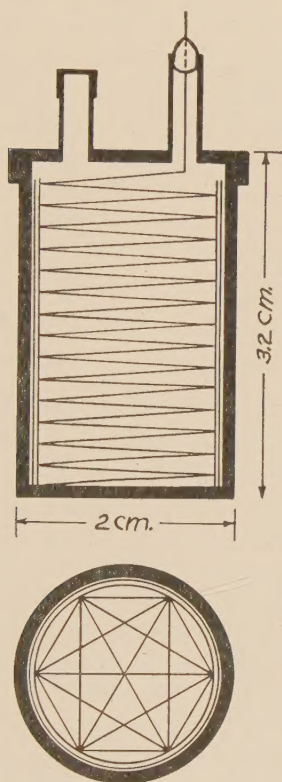
The calorimeter "can" itself (Fig. 1) is made of gold-plated copper and has a capacity of about 8 cc. Two entrance tubes project from the top of it. One is provided with a cap which may be soldered on. It is used for loading and unloading. The other has a copper platinum seal in the outer end of which is fused a soft glass bead. Through this a platinum wire leads to the heating coil. The heating unit itself is a lattice-work of 0.002 inch platinum-iridium wire which is suspended on a mica cylinder. It has a resistance of about 100 ohms at room temperature and about 80 ohms at liquid air temperature. The end of the coil is soldered to the inside of the can which thus serves as the second lead to it.

The can as a whole is suspended by three threads which lead out through holes in the top of the shield, thus enabling one to raise it into position after all electrical connections have been soldered.

The shield (Fig. 2) is a copper cylinder (4×11.5 cm.) closed at the top and fitted with a lid at the bottom. It is wound on the outside with a constantan heating resistance in such a manner that the heat is distributed evenly over the whole surface. Heating and thermocouple leads are wound around a tightly fitting inner sleeve several times, the whole soaked with liquid Bakelite, slipped into place and baked at 110 degrees until hard. Any heat leaking down the wires from the outside is thus taken up by the shield. This method

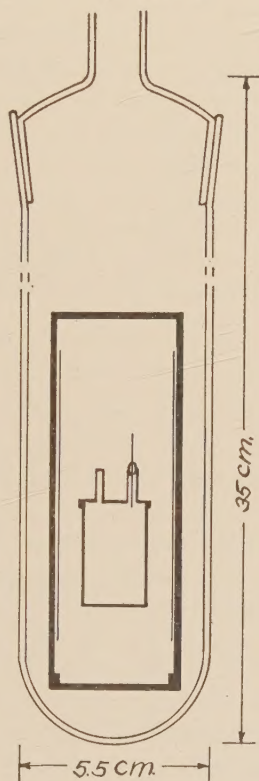
is preferred in this case to the usual one, namely, the use of a heavy block of metal at the top, because the latter causes lags in the change of rate of heating and thus makes it difficult to maintain adiabatic conditions.

FIG. 1.



Calorimeter can.

FIG. 2.



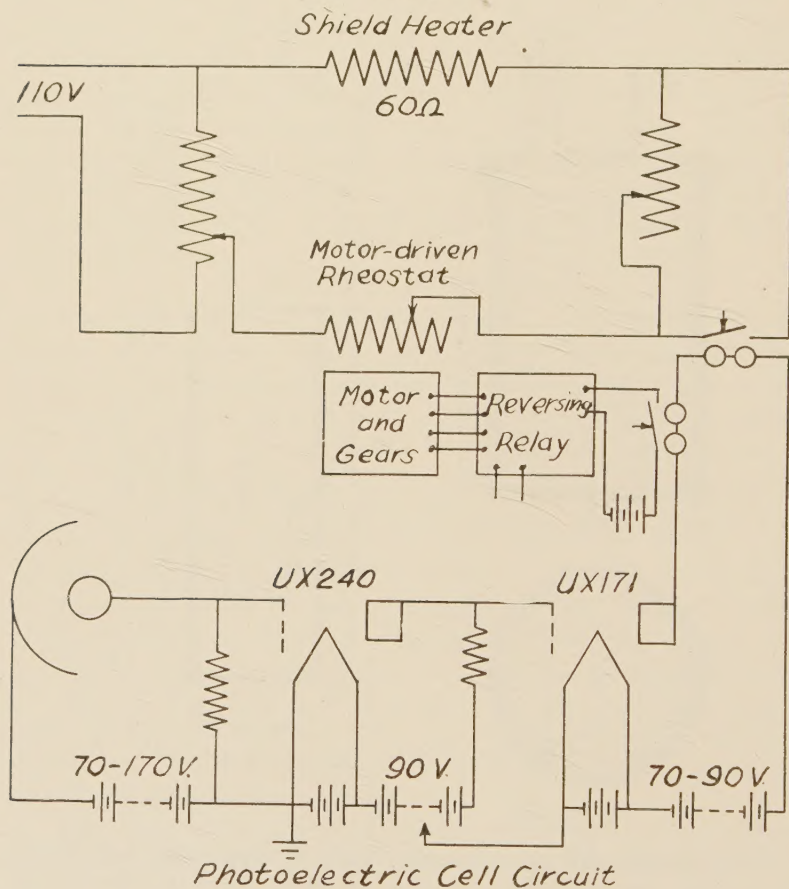
Calorimeter shield and vacuum system.

The shield with calorimeter inside is suspended in a large glass tube connected by a ground glass joint to the usual vacuum system. All the wires are led out through a De Khotinsky seal.

Adiabatic conditions are maintained by the following arrangement. A difference thermocouple between the can and the shield is connected directly to a sensitive mirror galvanometer which operates a photo-electric-cell-relay device

described by us in a previous paper.⁶ This operates a reversing relay controlling a motor driven rheostat which regulates the current flowing through the shield heating circuit as shown in Fig. 3. The deflections of the galvanometer which

FIG. 3.



occur in actual practice correspond to a temperature variation of $\pm 0.05^\circ$. The calorimeter may be operated successfully by hand control if such a system is not available.

⁶ Southard and Andrews, *JOUR. FRANK. INST.*, 207: 323 (1929).

TEMPERATURE MEASUREMENT.

The temperature was observed by means of a copper-constantan thermocouple which was soldered to the outside of the can at the same point as was the difference thermocouple. This had been compared with a Bureau of Standards platinum resistance thermometer at sixteen points between the boiling point of liquid oxygen and the melting point of ice with the aid of a thousandth degree low temperature thermostat.⁷ Comparisons were made at intervals of ten to fifteen degrees, and a temperature e.m.f. scale accurate to 0.01° constructed. Hence little, if any error can arise from this source. This is confirmed by the fact that the fusion temperature of toluene was found to be within 0.01° of that reported by Kelley⁸ and that obtained at Leiden,⁹ indicating a good agreement among the three temperature scales, in this range, at any rate.

MEASUREMENT OF HEAT INPUT.

The energy input in calories was calculated from the equation $H = 0.23912 EIt$. The potential drop E across the can heating coil was measured on a Leeds and Northrup recording potentiometer. Actually less than 50 mv. was measured by this instrument. The remainder, amounting to two to three volts was opposed by a constant accurately known e.m.f. as shown in the circuit in Fig. 4. R_1 and R_2 are Leeds and Northrup resistance boxes, and the one ohm coil was checked with one which had been calibrated by the Bureau of Standards. R_1 and R_2 always were set to total 1000 ohms connected by a heavy copper bar and a current of 5 ma. was easily maintained to 0.01 per cent. by checking the drop across the one ohm coil every thirty minutes. This was possible in part because all batteries in the measuring circuits were kept at nearly a constant temperature. The fractional part of the 1000 ohms set in R_1 determined the amount of the known constant opposing e.m.f. in the recording potentiometer circuit. By this means the range of the recorder was tremendously increased and an accuracy of one

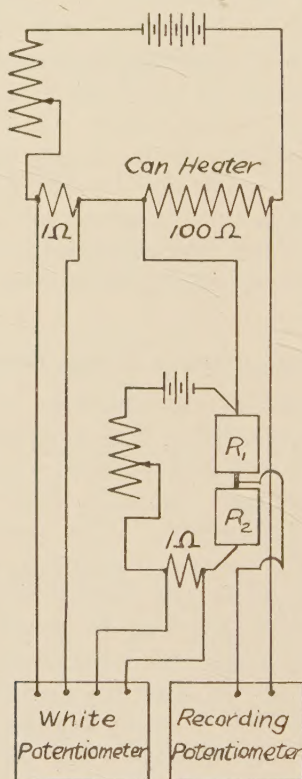
⁷ Southard and Andrews, *loc. cit.*

⁸ Kelley, *J. A. C. S.*, **51**: 2739 (1929).

⁹ *Com. Phys. Lab. Univ. Leiden*, No. 157.

part in 5000 was obtained. In certain cases a L. & N. type "K" potentiometer was employed using two standard cells in series, but the first method gave sufficiently accurate results and not only had the advantage of being semiauto-

FIG. 4.



Heating circuit.

matic but also provided a continuous curve showing the potential drop at any instant.

The current through the can heater was measured by observing the potential drop across a 0.1 ohm coil in series with it on a White potentiometer. By using a 45 volt battery with several thousand ohms in series, a current of about 25 ma. was obtained which varied in a slow and regular manner. The possible accuracy of this measurement was one in several

hundred thousand but in actual practice it was read to one part in ten or fifteen thousand. The time of heating on each observation was about twenty minutes, the stop watches were found to be accurate to about $1/5$ second over this period. Hence, the total error due to energy measurement should not be over 0.05 per cent. after a small correction for the leads from the can to the shield is taken into account.

METHOD OF OPERATION.

A sample of material is weighed into the calorimeter can, the latter soldered shut and tested for leaks by placing it in the vacuum system for three or four hours and then reweighing. The heating leads and thermocouples are then soldered on and the can raised into position in the shield as mentioned above. The outer glass casing is put on, the system evacuated, refilled with hydrogen and a dewar of liquid air brought slowly up around it. In less than an hour liquid air temperature is reached. The system is then evacuated and a current of about 25 ma. started through the calorimeter heating unit causing the temperature to rise about $1/3$ degree per minute. The heating of the shield is controlled by hand until its temperature is rising at the same rate as that of the can as is shown by a continued zero deflection of the galvanometer in the difference thermocouple circuit. It is then switched over to the photoelectric cell device. When this has been accomplished, the temperature is read and a stop watch started simultaneously. Since the temperature is rising continually, it is convenient to set the potentiometer dials at an e.m.f. slightly higher than the true e.m.f. at the time and wait, stop watch in hand, until the image from the galvanometer mirror crosses the zero point, at which time the stop watch is started. At the end of about twenty minutes this procedure is repeated except that the watch is stopped. If two watches are used, the second may be started at the same instant that the first one is stopped and so on. When the melting point is reached naturally the rate of temperature increase rather abruptly becomes zero (if the compound is pure) and the current through the shield heating coil has to be quickly readjusted by hand.

The current through the calorimeter coil is read every ten

minutes and the potential drop read from the recorder at leisure. When the run is completed the weight of material is checked, and any variation in the weight of solder used is determined and taken into account in the calculations. The error from this source is probably a matter of a tenth of a per cent. but of course this can be greatly reduced by using a larger calorimeter.

MATERIALS USED.

The benzene used was a "thiophene free C.P." sample which had been further purified by distillation from sodium. The octanol-1 was purchased from the Eastman Kodak Co. and cut on a six foot column vacuum still by G. B. Malone. B.P. 104.5 to 104.6° C. at 25 mm. A freezing point curve showed the M.P. to be -15.6° C. and impurities to be present amounting to around one per cent. The octanol-4 was prepared and purified by E. E. Reid and co-workers. It boiled at 81.3° C. at 20 mm. and a freezing point curve showed impurities amounting to around 10 per cent. Of course the work on this substance could be used for comparative purposes only. The toluene was a sulphonic acid derivative purchased from the Eastman Kodak Company. It was cut on a three foot fractionating column and boiled over a range too small to be visible on an Anschütz thermometer. No sulfur could be detected on treatment with conc. sulfuric acid. A time-temperature freezing curve showed it to be of extreme purity as did also the lack of any extensive premelting.

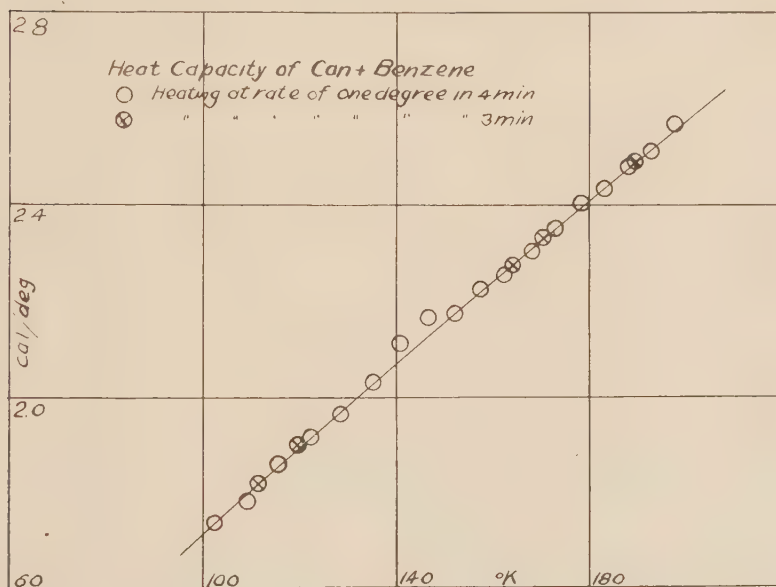
RESULTS.

An adiabatic condition is maintained on an average as is shown by the fact that the heat of fusion was found to be 1584 cal. at 177.94° K. which is within 0.2 per cent. of the mean value found by Kelley¹⁰ using a modification of the Nernst type calorimeter. This value is within the limit of his average deviation. A constant heat leak due to faulty difference thermocouples or temperature control apparatus should show up here quite definitely, in as much as the heat capacity of the empty calorimeter which is found by calibration with a compound of known heat capacity, does not enter into the calculation of the heat of fusion. Linear equations which held quite well for the heat capacities for some distance

¹⁰ Kelley, *loc. cit.*

above and below the melting point were integrated and the observed heat input in the region of fusion corrected in a purely analytical manner. A correction for the resistance of the leads amounts to .9 cal. This may be in error by 0.3 cal. In this case the calorimeter held the fusion temperature $\pm 2. \mu v$ for over an hour and was in the fusion region for a total of about two hours. The fusion temperature reported was held within $0.1 \mu v$, the limit of the accuracy of observation, for more than forty minutes of this. Obviously, a heat leak over this period of time concentrated, so to speak, into one reading would certainly make itself evident.

FIG. 5.



That equilibrium is maintained within the calorimeter to a satisfactory degree is shown by the fact that a constant rate for temperature increase is attained within one-half minute after the current is turned on. In this time the temperature has risen about $1/6$ of a degree. If the whole heat capacity curve were displaced by as much as one-half of this value the error would hardly be noticeable. Also a change of about thirty per cent. in the rate of heating does not displace the curve appreciably as is shown in Fig. 5.

FIG. 6.

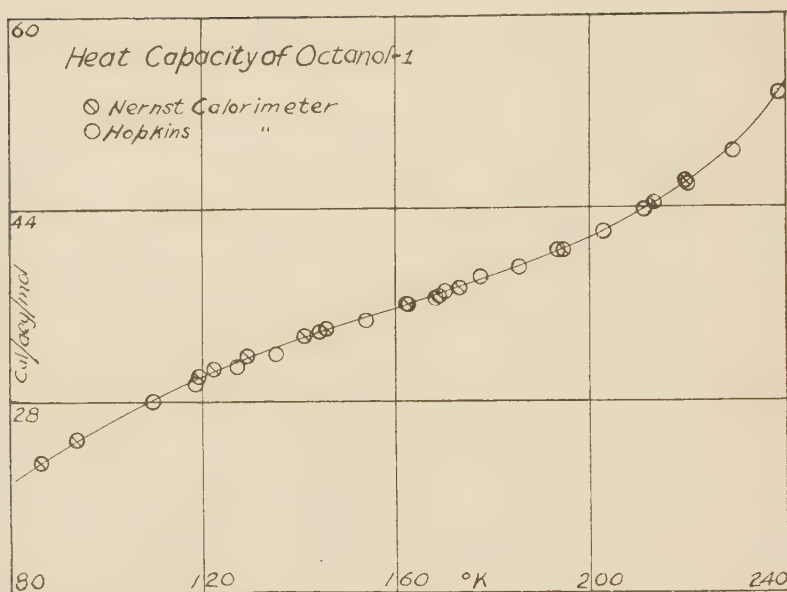
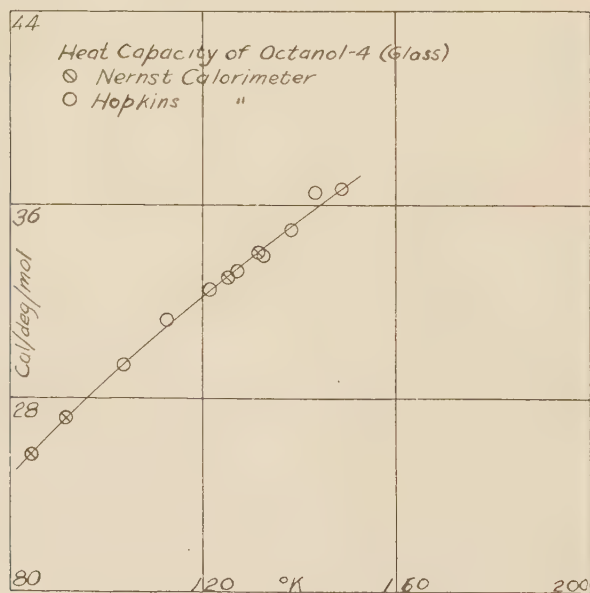
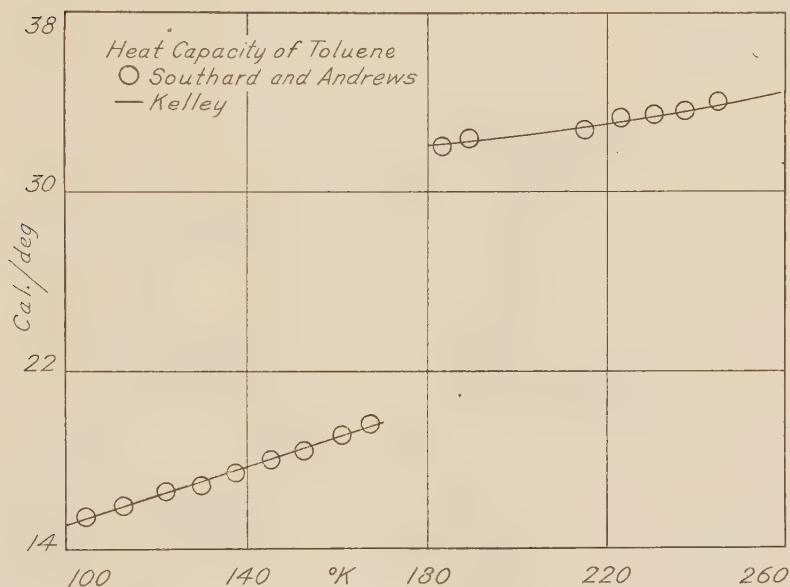


FIG. 7.



To compare the results obtainable with this adiabatic calorimeter with those of the Nernst type, the heat capacities of benzene, octanol-1 and octanol-4 were determined in the calorimeter described by Andrews.¹¹ These same three compounds were then run in the adiabatic calorimeter. Using benzene as the reference compound, Figs. 6 and 7 show the agreement obtained. The absolute values are probably somewhat high and are not to be taken as final although those for benzene are only about half of a per cent.

FIG. 8.



higher than Nernst obtained.¹² This is largely due to the fact that the steel joint in the vacuum bomb had become somewhat defective and the proper vacuum could not be maintained. The heat of fusion of octanol-1 and octanol-4 could not be accurately determined because of the large amount of impurities present.

Using some recently obtained unpublished values of G. S. Parks for the heat capacity of benzene as a reference com-

¹¹ Andrews, *JOUR. FRANK. INST.*, **206**: 285 (1929).

¹² Nernst, *Ann. d. Phys.* (4), **36**: 395 (1911).

pound, lowers these values several per cent. With the calorimeter calibrated on this basis the following values are obtained for toluene. (Fig. 8.)

Heat Capacity of Toluene.

Crystals.		Liquid.	
Temp. K.	C_p , cal./mol.	Temp. K.	C_p , cal./mol.
104.25.....	15.50	18.38.....	32.00
112.60.....	15.90	189.25.....	32.40
121.97.....	16.55	217.17.....	32.75
130.00.....	16.73	223.14.....	33.3
137.44.....	17.38	230.21.....	33.42
145.23.....	17.98	237.58.....	33.6
152.72.....	18.41	244.79.....	34.1
160.34.....	19.11		
167.35.....	19.61		

Comparison of these values with those of Kelley, who used the same type calorimeter and method as Parks, shows satisfactory agreement.

The authors express their appreciation of the valuable assistance given them by Mr. Teets in determining the time-temperature curves mentioned above, and of the kindness of Mr. R. H. Smith in preparing for them the remarkably pure sample of toluene.

SUMMARY.

1. An adiabatic calorimeter for heat capacities at low temperatures has been devised which gives results consistent to about 1/2 per cent.

2. It is faster and simpler in operation, more economical than the present most used type and applicable to a wider range of organic compounds because of its small size (8 cc.).

3. The heat of fusion of toluene was found to be 1584 calories/mol. at 177.94° K.

4. The heat capacity of toluene was found from 100° K. to 250° K. by comparison with benzene.

The author of this dissertation, John Campbell Southard, was born September 14, 1906, at Willard, Ohio. He received his early education in the public schools of East Cleveland, Ohio, and attended Berea High School for three years. In 1927 he received the degree of Bachelor of Science in Chemistry from Baldwin-Wallace College, Berea, Ohio. Since that time he has been in attendance in the Graduate Chemistry Department at The Johns Hopkins University.

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